Spectroscopic and conductivity study of Zinc phthalocyanine

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Abstract:

Zinc phthalocyanine was prepared and charactarized by IR and uv-visible spectra. The effect of trichloroaceticacid (TCA) on zinc phthalocyanine show the ability of TCA to demetalation (Zinc phthalocyanine change to free phthalocyanine) and these result consider a new method to prepare H_2Pc. Ir spectra of the complex recorded before and after treating with TCA to compare and charactrize the metal depended bands. The conductivity of doped ZnPc is more than the conductivity of undoped and the conductivity increase with the concentration of TCNQ.

الخلاصة:

حضر فثالوسيانين الزنك وشخص باستخدام مطيافية الاشعة تحت الحمراء ومطيافية الأشعة فوق البنفسجية- المرئية. كذلك درس تأثير ثلاثي كلوروحامض الخليك (TCA) على تركيب فثالوسيانين الزنك واتضح بان له القدرة على إزالة الفلز وتحويل فثالوسيانين الزنك إلى فثالوسيانين الحر وتعد هذه طريقة جديدة لتحضير الأخير. دراسة الأطياف الالكترونية تبين التأثير القليل للمذيب على أطياف فثالوسيانين الزنك. قورن طيف تحت الحمراء لفثالوسيانين الزنك قبل وبعد معاملته بثلاثي كلوروحامض الخليك لغرض تشخيص الحزم التي تعتمد على الفلز. بينت الدراسة أيضاً تأثير التشويب بتراكيز مختلفة بـ TCNQ ولوحظ زيادة التوصيلية بصورة طردية مع زيادة تركيز المادة المشوبة.

Introduction:

phthalocyanines and its derivatives are interesting compounds for various application. Dyes, catalysts, solar cells, photosensors etc. The electrical properties of phthalocyanines depend very much on the macrocyclic systems. Good semiconducting or conducting properties can be achieved by different method such as polymerization via central metal atom such as Co, Ru … where the π-π overlap of the perpendicular orbitals is achieved. Doping of the macrocycles generates charge carries leading to semiconducting phthalocyanines [1, 2].

Metallophthalocyanines are charactrized by an intense band near 350 nm (sort band or B-band) and another intense band near 700 nm (Q-band) and these band depend very much on the solvents. Metal free phthalocyanine differ in having an interence doublet bands near 700 and 665 nm[4]. Because of the large size and complexity of the phthalocyanine molecules the assign of the infra-red spectra is more difficult. However the eariler work depend very much on the characteristic finger print of the ligand[4, 5].

Recently the preparation, charactrization of ZnPc and the effect of TCA on the structure and the effect of TCNQ as a dopant on the conductivity will investigated.

Experimental:

Solvents were dried and distiled before use. All other chemicals were used as received from Aldrich Chemicals Co. IR spectra were recorded as KBr disk on a pye-unicam SP3-300S. uv-visible spectra were recorded by Cintra-5- spectrometer using 1 cm quartz cell. The electrical conductivity was measured by two probe methode on apressed disk (1.3 cm and thickness of 1-2 mm) which obtained by using pye-unicam die with a pressure of ~ 108 pascal. The disks were painted on to each face using silver paint(6).

Preparation of Zinc phthalocyanine:

ZnPc was prepared by Barrett et al method(3). 1.28 g. of phthalonitrite (1,2 dicyanobenzene) and 0.13 g. of zinc dust were heated slowly to 250-270 oC for 15 min. the product was cooled to room temperature ground and boiling with dilute HCl (1M) to remove any unreached zinc then filtered and washed with ethanol and dried at 100oC for 3 hrs. (yield 64% of therotical) as a blue powder.

Doping of ZnPc:

Doped of ZnPc carried out by the following method( ) ZnPc and TCNQ with mole ratio 1: 0.5 and 1:1 were suspended in acetone, stir at ~ 50oC for 3 hrs. then cooled to room temperature and evaporate the acetone and dried at room temperature(5).

Results and Discussion: In general normal metallophthalocyanines exist in different form namely α, β and γ(x) form depend on the method of preparation for example α form prepared by recrectilization of CuPc from Conc. H2SO4(7). The β form is more stable form, in this case IR spectroscopy is a useful method to distinguish between these forms. IR spectra of ZnPc show in Fig. 1 this result is identical with the β form. To decide which bads in the spectra are metal depended the ZnPc boild with trichloroaceticacid (TCA) for 1 hr, the colour ZnPc change from dark blue to green powder and the spectra of the later (Fig. 1). the disappear of band in the later at 995, 920 and 890 cm-1 give evidence that these bands attributed to metal ligand vibration and the ZnPc change to metal free phthalocyanine.

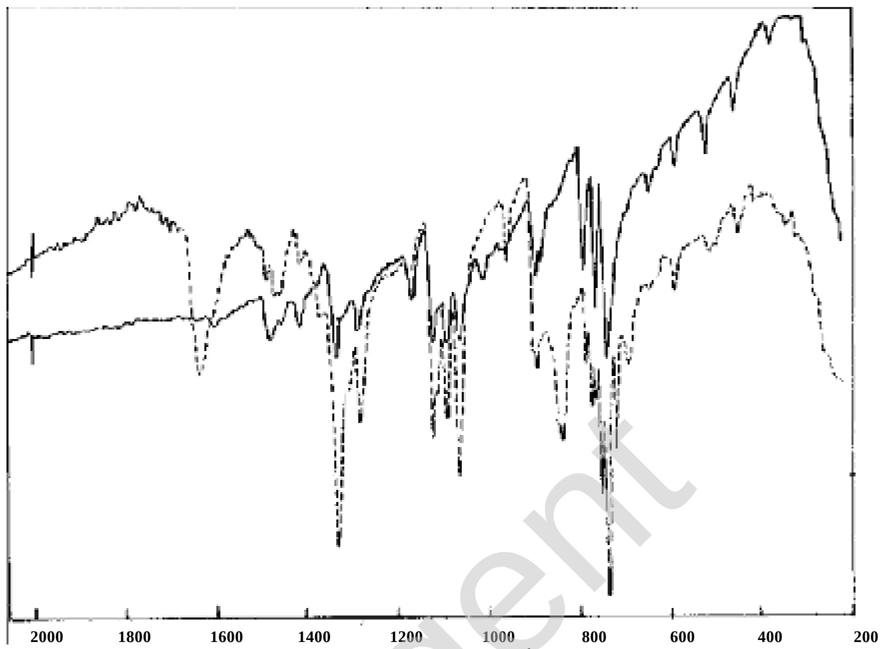

Fig. 1: The IR spectra of ZnPc before (———) and after (- - - - - -) boiled with TCA

UV-visible:

The uv-visible data of ZnPc are summarized in Table 1 and Fig. 2. The spectra in all solvents show an intense absorption band at 668-685nm, these bands assign as a Q-band (π-π^*). When compared the spectra in methylnaphthalene as a inert solvent and pyridine as a coordinat solvent a blue shift was observed in the pyridine due to complex formation between pyridine and ZnPc.

Table 1
UV-visible spectra data of ZnPc in different solvents

Solvent	Q-band λ_{max} nm (log ε)	B-band λ_{max} nm (log ε)	Other band
Pyridine	672 (5.45)	347 (4.8)	646 (4.56), 607 (4.5)
Methyl-naphthalene	685 (5.04)	345 (4.92)	650 (4.42), 613 (4.5)
DMF	668 (4.41)	340 (4.38)	604 (4.09)

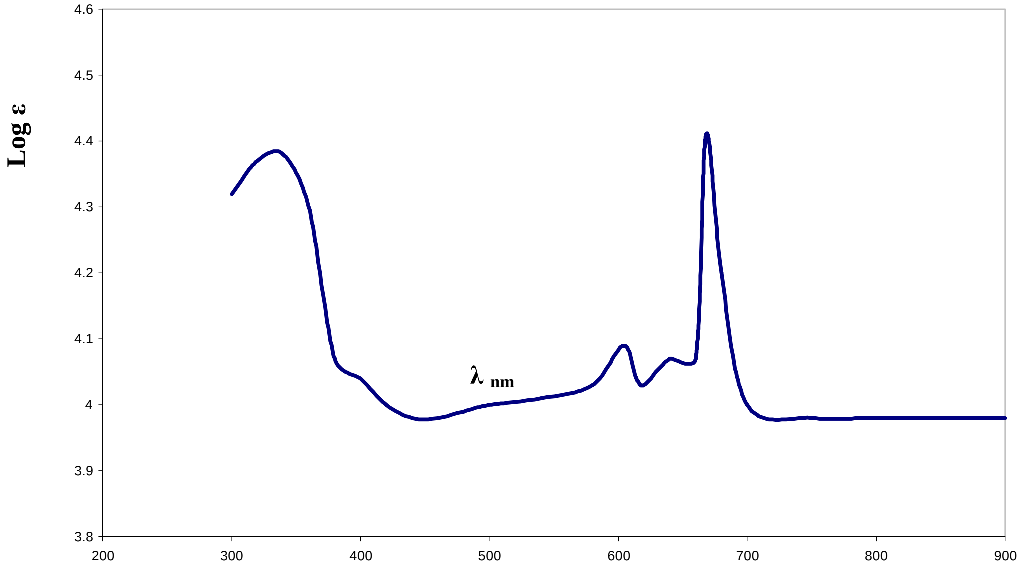

Fig. 2: Electronic absorption spectra of ZnPc in DMF

DC. conductivity:

D-C conductivity of the samples were carried out under atmospheric pressure and at temperature range from 30-100^{o}C. The undoped ZnPc exhibits electrical conductivity about 5 x 10^{-10} s/cm at 30^{o}C. Fig. 3 shows that the conductivity increases by up 2-5 orders of magnitude as compared to undoped ZnPc where the conductivity increase with increase the concentration of TcNQ.

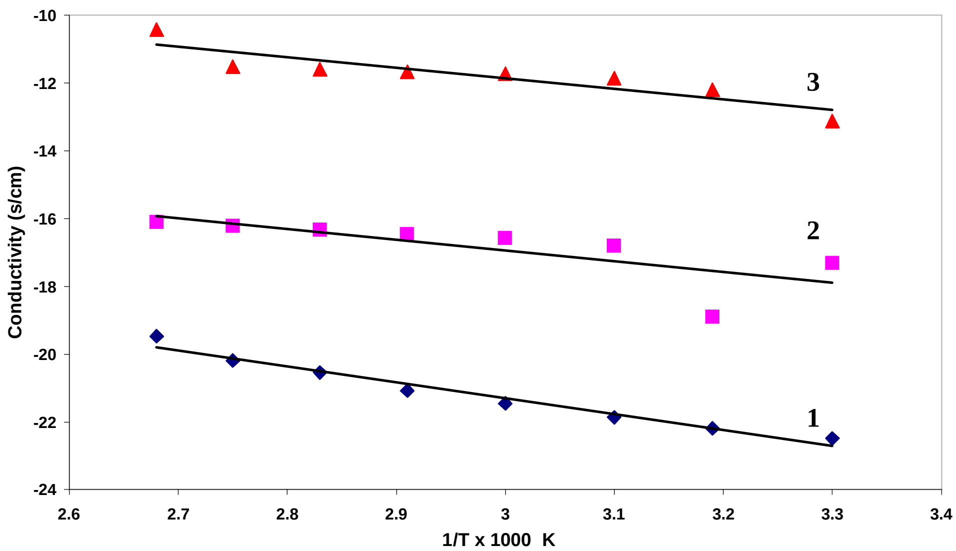

Fig. 3: Conductivity vs temperature for (1) ZnPc , (2) 1:0.5 ZnPc:TCNQ (3) 1:1 ZnPc:TCNQ

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